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THE BRANCHING REACTION AND CHAIN TRANSFER IN STYRENE POLYMERIZATION

MAURICE MORTON

UNIVERSITY OF AKRON

FEBRUARY 1954

Statement A
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THE BRANCHING REACTION AND CHAIN TRANSFER IN STYRENE POLYMERIZATION

MAURICE MORTON

UNIVERSITY OF AKRON

FEBRUARY 1954

AERONAUTICAL RESEARCH LABORATORY

CONTRACT No. AF 33(616)-337

PROJECT No. 7340

TASK No. 70325

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This is the first annual report issued by the Rubber Research Laboratory, University of Akron, describing work performed under Contract No. AF 33(616)-337. The work was performed under Project No. 7340, Rubber, Plastic, and Composite Materials, Task No. 70325, Branching in High Polymers, with Dr. Leonard Spialter of Chemistry Research Branch, Aeronautical Research Laboratory, acting as WADC Task Scientist. This report is one of a series to be issued on this project; others will follow as the research progresses.

ABSTRACT

The chain transfer activity of the following four compounds in the polymerization of styrene was measured: t-butyl mercaptan, t-butyl alcohol, isopropyl cyanide and isopropyl alcohol. This work was intended to measure the relative ease of formation of certain sulfur-, oxygen-, or carbon-headed free radicals and thus to establish the relative activity of these radicals in abstracting hydrogen from a given compound, as it may apply to the formation of branches on a polymer chain.

The following values were obtained for the rate expressions for the transfer reaction between a styrene radical and each respective compound:

t-Butyl Mercaptan	1.0×10^6 exp 4400/RT
t-Butyl Alcohol	4.2×10^6 exp 13800/RT
Isopropyl Cyanide	2.0×10^6 exp 10400/RT
Isopropyl Alcohol	1.9×10^{10} exp 19800/RT

The above values appear to offer evidence that it is the hydroxyl hydrogen in the t-butyl alcohol which undergoes chain transfer. However, more substantiating evidence will have to be obtained before any definite conclusions can be drawn concerning the type of free radical which is formed from these compounds.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



LESLIE B. WILLIAMS

Colonel, USAF

Chief, Aeronautical Research Laboratory

Directorate of Research

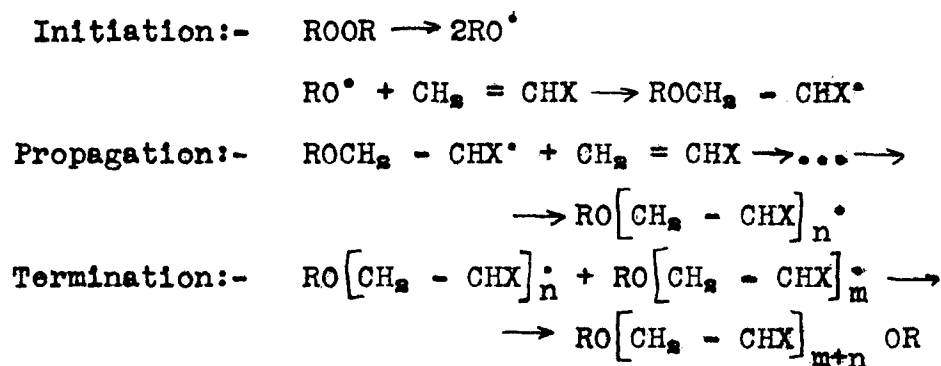
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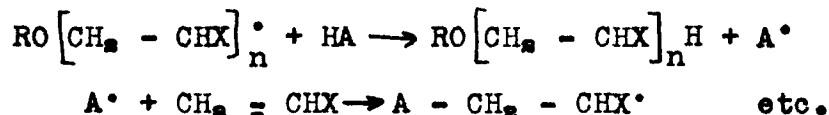
INTRODUCTION

In the process of addition polymerization the polymer chain is built up by rapid successive additions of the monomer molecules to an active growing chain, commonly of the free radical type. In this process three basic steps have been established and are generally accepted to-day. These are known as the initiation, propagation and termination steps, and are a characteristic of all addition polymerization reactions. Using as an illustration the polymerization of a vinyl compound by the free-radical decomposition of a peroxide, these steps can be represented as follows:-



The termination step above is represented as a recombination of the growing free radical chains. It has been shown that termination can also occur by a disproportionation reaction leading to two terminated chains.

In addition to the three basic steps illustrated above, it is possible to have various transfer reactions in which the free radical activity may be transferred from the growing chain to some other molecule. This may be represented as follows:



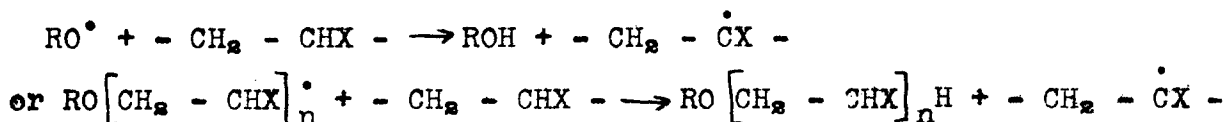
The molecule HA may be present as a solvent or an impurity, and must contain a sufficiently labile hydrogen atom (H), or some other similar atom, to participate in the transfer step. If the resulting free radical (A^{\bullet}) is sufficiently reactive to initiate a new chain, then the transfer step merely affects the molecular weight of the final chains, without affecting the overall rate of the polymerization. Otherwise, the transfer step may result in retardation, or even inhibition, of the polymerization. The chain transfer rates of a number of systems have been studied.

In the special case where HA represents a polymer molecule, then any growth of the free radical, A^{\bullet} , will lead to a branched polymer chain (unless the transfer should fortuitously occur with a hydrogen on a terminal carbon atom of the polymer molecule). This type of reaction is generally considered as being responsible for the formation of branches in a polymer chain. It should be noted that this type of reaction should not be confused with the cross-linking reaction, which can only occur in the presence of residual double bonds in the polymer chain. In that case a growing free radical adds directly to the double bond in the polymer molecule and can continue the propagation step by reacting with other double bonds, either in monomer or in polymer molecules. This type of reaction can rapidly lead to the formation of "infinite" networks, which cease to be distinguished as individual polymer molecules. The branching reaction, on the other hand, does not depend on the presence of double bonds in the polymer chain, and cannot, by itself, lead to the formation of large networks; although it undoubtedly will alter the molecular weight distribution of the system. The kinetics of the cross-linking reaction can be determined experimentally, because of the presence of a measurable criterion, viz.

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the formation of an infinite network (gelation): and this has already been done in this laboratory in the case of butadiene polymerization. The branching reaction, however, has not as yet yielded to a kinetic analysis, mainly because of the lack of any criterion for the extent of branching. Furthermore, reliable physical or chemical methods for the determination of branching in high polymers are not available as yet.

In any given homopolymerization, the branching reaction could be initiated by two possible steps. Using the case of peroxide-catalyzed free radical polymerization of a vinyl compound as an illustration, the two possible steps can be shown as follows:



Thus the attacking radical could be either an initiator radical or a chain radical. If it happens to be the latter, then the extent of the branching reaction would be independent of the type of initiator used in the polymerization. However, if branching is largely initiated by the initiator radical itself, then the type of initiator used would be a very important factor governing the extent of branching. Since a wide variety of initiators is available, it is of great importance to determine this effect of different initiators on the branching reaction. As a starting point, it might be of great interest to obtain a measure of the chain transfer activity of the different types of radicals. These might include the three principal types, i.e. oxygen -, carbon -, and sulfur-headed free radicals, which might be expected to show considerable differences. If a method of evaluating the extent of branching in the polymer chain were available, then a study of the polymerization initiated by these different

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types of radicals would be sufficient to yield the desired information. However, in the absence of such a method, some other approach must be tried.

The approach used in this work was to study the lability of a given hydrogen atom in four compounds, viz. t-butyl mercaptan, t-butyl alcohol, isopropyl cyanide and isopropyl alcohol. This was done by determining the chain transfer efficiency of these compounds in the bulk polymerization of styrene. Such measurements could be useful in predicting the relative activity of the corresponding free radical in abstracting a hydrogen atom from a given molecule. Thus, for example, if it is known that it is the hydroxyl hydrogen in t-butyl alcohol which undergoes chain transfer with a polystyrene free radical, then the chain transfer activity of the alcohol would be an inverse function of the chain transfer activity of the corresponding radical, $(\text{CH}_3)_3\text{CO}^\bullet$. In this way the relative activity of a series of radicals can be estimated from the relative chain-transfer activity of the corresponding compounds towards a reference radical, in this case the polystyrene radical.

Although some qualitative measure of the reactivity of the given hydrogen atom in these compounds may be available, very little quantitative data are known. Such data may throw some light on the question concerning the effect of different initiators on the structure of the polymer chain.

EXPERIMENTAL PROCEDURES

Materials

Dow styrene was distilled under nitrogen through a 200 mm Vigreux column to give a product which boiled at 46°C (20 mm Hg). This styrene was stored under nitrogen in a refrigerator. The nitrogen used through-

out was Airco high purity.

Eastman t-butyl mercaptan was distilled and the fraction with bp 66°C was used.

Eastman t-butyl alcohol was frozen and filtered at 20°C. The remainder melted at 25°C. This was filtered and 50% as solid was taken.

Isopropyl cyanide was prepared by the dehydration of isobutyramide. A mixture of 2.3 moles of the finely powdered amide and 2.4 moles of phosphorous pentoxide was heated. The nitrile began to come over almost at once. Vacuum was applied intermittently to reduce the time of the reaction. The crude nitrile was collected in a flask which was cooled by ice water. The nitrile was then redistilled over 10 g of phosphorous pentoxide, the fraction boiling at 101-102°C was again redistilled over phosphorous pentoxide and the fraction boiling at 101.5°C (n_d^{25} 1.3712) was taken.

Eastman isopropyl alcohol was distilled and the fraction with bp 81.5°C (n_d^{20} 1.3777) was used. The benzene used for viscosities was Baker's reagent grade.

Polymerizations

The polymerizations were carried out in one-ounce amber bottles with screw caps. The caps contained butyl gaskets which had been extracted with ethanol-toluene azeotrope. The required amount of styrene and the transfer agent was added to each bottle and the bottles were flushed with nitrogen. The bottles were then placed in an oil bath maintained at the required temperature $\pm 0.2^\circ\text{C}$. The bottles were then removed at 4% conversion $\pm 0.5\%$ and coagulated in 200 cc of anhydrous methanol. The polymer was filtered, redissolved in 100 cc of benzene, and reprecipitated in 500 ml of methanol. The polymer was then filtered and dried in an oven at 105°C for four hours.

Viscosity and Molecular Weight Determination

The viscosity of each polymer solution was determined in a Ubbelohde dilution viscometer. The solutions were made up by dissolving 0.4 g of polymer in 100 cc of benzene. Two 20 cc samples were removed and dried in an oven for two hours at 100°C to determine the concentration of the solution. Another 20 cc sample was removed and used for the first viscosity determination. Two subsequent dilutions were then made for viscosity determinations. A plot of η_{sp}/c vs. c and $\ln \eta_r/c$ vs. c gave the intrinsic viscosity when extrapolated to zero concentration. A typical plot is shown in Figure I.

From the intrinsic viscosity values, the number-average molecular weights were calculated by means of the following equation:-

$$\bar{M}_n = 167,000 [\eta]^{1.37} \quad (1)$$

The above equation was suggested by Mayo et al¹ from a comparison of viscosity and osmotic pressure data.

RESULTS

The transfer constants for each of the four compounds used in the polymerization of styrene were obtained in the usual manner² from the relation

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_T \frac{S}{M} \quad (2)$$

where \overline{DP} = number-average degree of polymerization of the polymer obtained in presence of the solvent

\overline{DP}_0 = number-average degree of polymerization of the polymer obtained in absence of solvent.

S/M = molar ratio of solvent to monomer

C_T = transfer constant, i.e. k_{tr}/k_p where k_{tr} is the rate constant for the transfer reaction and k_p is the propagation rate constant.

Since the above equation reflects an instantaneous relation, the polymerizations were restricted to very low conversions in order to avoid the complications of concentration changes. Values for the degree of polymerization were calculated from the intrinsic viscosity data using equation 1, and $1/\overline{DP}$ plotted against S/M, the slope of the resulting line yielding the value of the transfer constant. The plots obtained with the four compounds studied at two different temperatures are shown in Figures 2, 3, 4 and 5. Very good linearity was obtained in these plots, as shown. Furthermore, as a sign that the compounds studied did not behave as retarders, the rate of polymerization was measured at several solvent-styrene ratios. The only effect noted was the expected dilution effect on the second-order reaction rate. A typical plot is shown in Figure 6.

From the slopes of these lines, the transfer constant, C_T , was calculated for each of the four compounds. The values are shown in Table I. In addition, from the temperature coefficient of the transfer constant, it was possible to calculate the difference between the activation energies of the transfer and propagation reactions ($E_{tr}-E_p$). These are also listed in Table I.

TABLE I
Transfer Constants in Styrene Polymerization

<u>Compound</u>	<u>Transfer Constant (C_T)</u>			<u>$E_{tr}-E_p$ (kg cal.)</u>
	<u>60°C</u>	<u>100°C</u>	<u>130°C</u>	
t-Butyl Mercaptan	3.1	1.8	-	-3.4
n-Butyl Alcohol	-	5.5×10^{-5}	1.0×10^{-4}	6.0
Isopropyl Cyanide	-	2.7×10^{-4}	3.5×10^{-4}	2.6
Isopropyl Alcohol	-	7.9×10^{-5}	2.7×10^{-4}	12.0

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The values obtained for the transfer constant of the mercaptan agree quite well with those obtained by Mayo et al³. As expected, the other three compounds show a very low value for the transfer constant. At the temperatures studied, the transfer activity of these compounds decreases in the following order, isopropyl cyanide, isopropyl alcohol and t-butyl alcohol.

The above results become more significant if they are used to calculate the actual rate constant of the transfer reaction (k_{tr}). This can be done, since the propagation rate constant (k_p) for styrene is known. Using the value given by Matheson et al⁴ i.e. $k_p = 2.2 \times 10^7 e^{-7800/RT}$, it was possible to calculate the absolute values for the transfer reaction rate constant. These values are shown in Table II below.

Table II

Absolute Values for Transfer Rate Constants

<u>Compound</u>	<u>Transfer Rate Constant</u>			<u>E_{tr} (kg cal.)</u>	<u>A</u>
	<u>(k_{tr} in l/mole/sec)</u>			<u>(1/mole/sec)</u>	
	<u>60°C</u>	<u>100°C</u>	<u>130°C</u>		
t-Butyl Mercaptan	496	1000	-	4.4	1.0X10 ⁶
t-Butyl Alcohol	-	.03	.13	13.8	4.2X10 ⁶
Isopropyl Cyanide	-	.16	.44	10.4	2.0X10 ⁶
Isopropyl Alcohol	-	.05	.34	19.8	1.9X10 ¹⁰

It is, of course, not possible to state unequivocally just which particular hydrogen atom in the above compounds undergoes the transfer reaction. This is especially so in the case of the alcohols, since it may be either the hydroxyl hydrogen or one of the hydrogens attached to a carbon atom. There are, apparently two schools of thought concerning this point. Bartlett⁵ favors rupture of a carbon-hydrogen bond rather than the oxygen-hydrogen bond in alcohol. However,

Steacie⁶, shows several mechanisms in which there is chain transfer between a free atom and the hydroxyl hydrogen of an alcohol. This point may possibly be decided by means of experiments utilizing the isotope effect, and it is planned in the very near future to carry out appropriate rate measurements involving deuterated compounds, for this very purpose.

However, it is of interest to examine the data in Table II in the light of this controversy, and to speculate on the significance of the results. For instance, the three tertiary compounds (t-butyl mercaptan, t-butyl alcohol and isopropyl cyanide) all show a high steric factor which is remarkably similar. This would seem to indicate the degree to which the three substituents on the central carbon atom shield the active hydrogen. Hence, in t-butyl alcohol, it would be difficult to suppose that one of the methyl hydrogens is being attacked, since such a high steric factor would then not be operative. The same reasoning can also be applied to the nitrile, where one would expect the tertiary hydrogen to be much more labile than one of the methyl hydrogens.

On the other hand, the activation energy values for the above three tertiary compounds indicate the actual reactivity of the particular bond which is broken. Here it is obvious that the order of reactivity decreases from the mercaptan to the nitrile to the alcohol, as shown by the increasing activation energy. This, too, can be taken as evidence that the respective bonds broken in the chain transfer reaction are the S-H, t-C-H and O-H bonds in the above three compounds. If any extent of reaction occurred with the methyl hydrogens, one would not expect such differences in activation energy, since all three compounds contain several methyl groups. The much higher activation energy of the isopropyl alcohol can also be taken as evidence that it

is not the methyl hydrogen which participates in the chain transfer step. Of course, in this case it may either be the hydroxyl hydrogen or the secondary hydrogen which reacts, or both. The reactivity of such a hydrogen atom could be expected to be lower than any similar hydrogen atom in the three tertiary compounds. It is interesting to note, too, that the isopropyl alcohol has a much lower steric factor, which would be expected in a compound where there is at least one hydrogen atom on the central carbon. This might be construed as evidence favoring the reaction of the hydroxyl hydrogen in this compound rather than the secondary hydrogen.

It must be concluded, however, that the evidence discussed above is not unequivocal, and that the decision as to which given bond is ruptured during a chain transfer reaction can only be decided by further experimental work. On that basis, although the chain transfer activity of the above compounds in styrene polymerization has been determined, there is as yet insufficient evidence to permit a decision as to what particular free radical is formed during such a reaction. Hence the activity of such free radicals in reuniting with hydrogen atoms (by chain transfer) will only be decided after such new evidence can be acquired.

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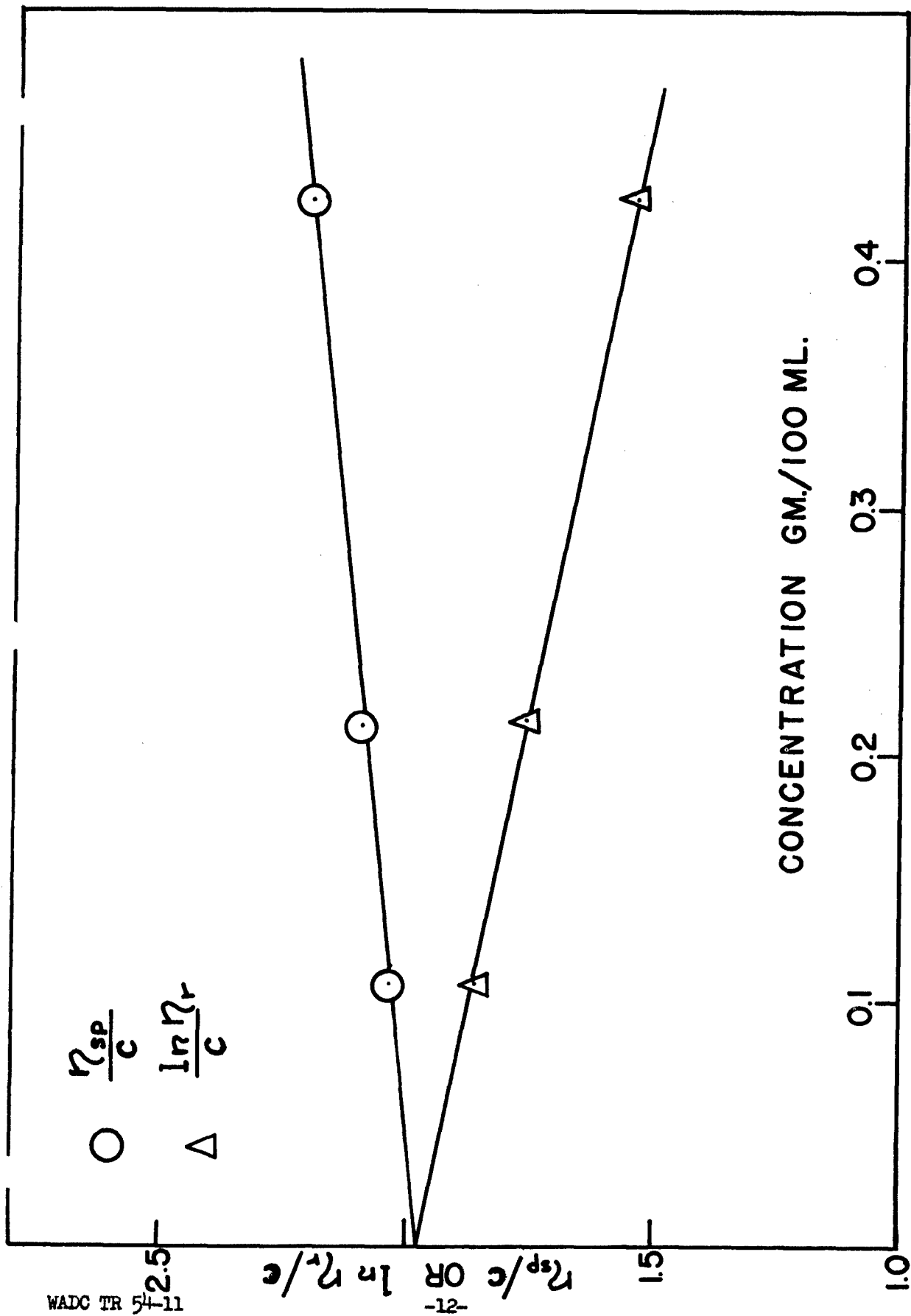
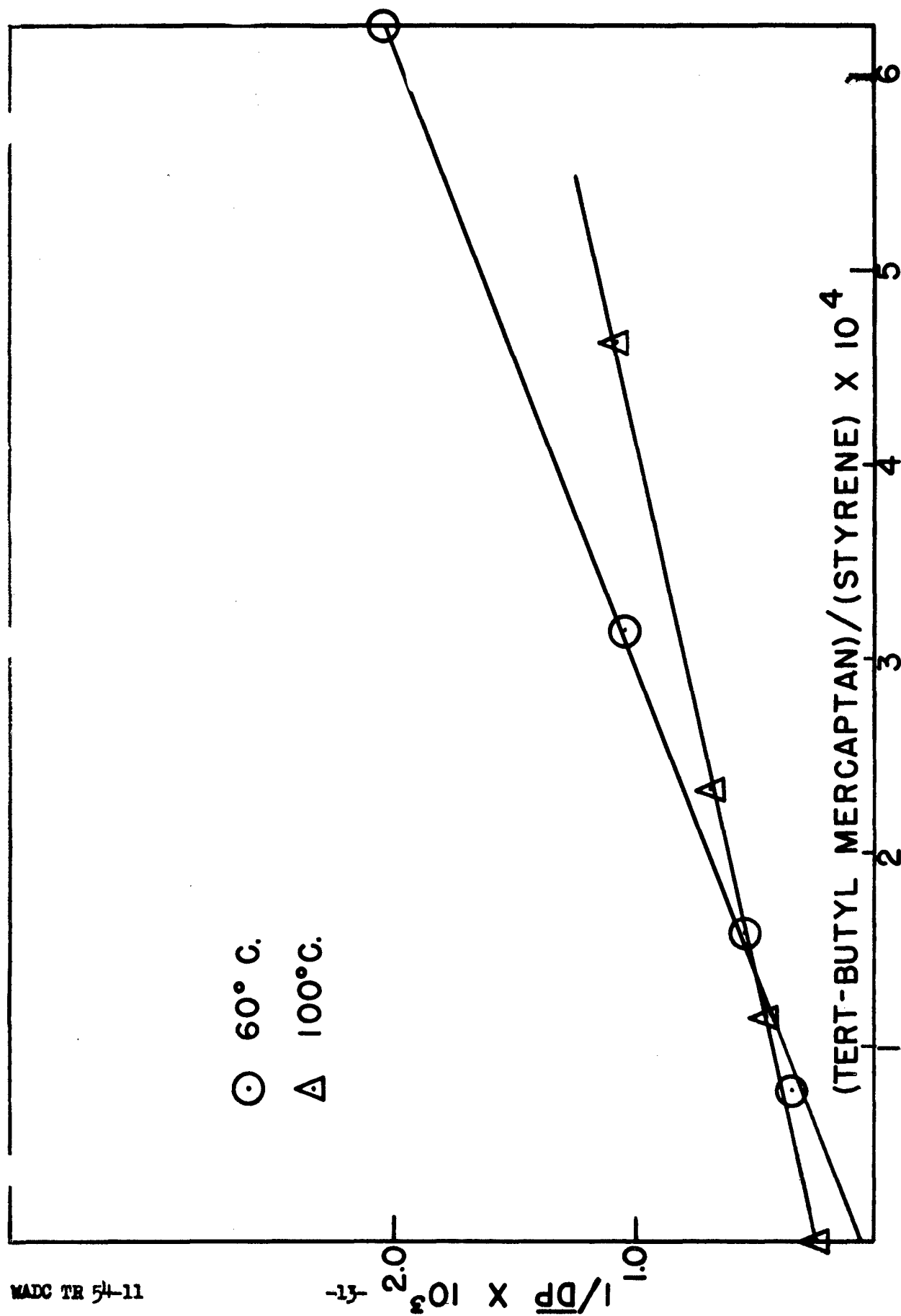


FIG.1. VISCOSITY-CONCENTRATION PLOT FOR POLYSTYRENE IN BENZENE

FIG. 2. EFFECT OF TERT-BUTYL MERCAPTAN ON THE $\bar{D}P$ OF STYRENE

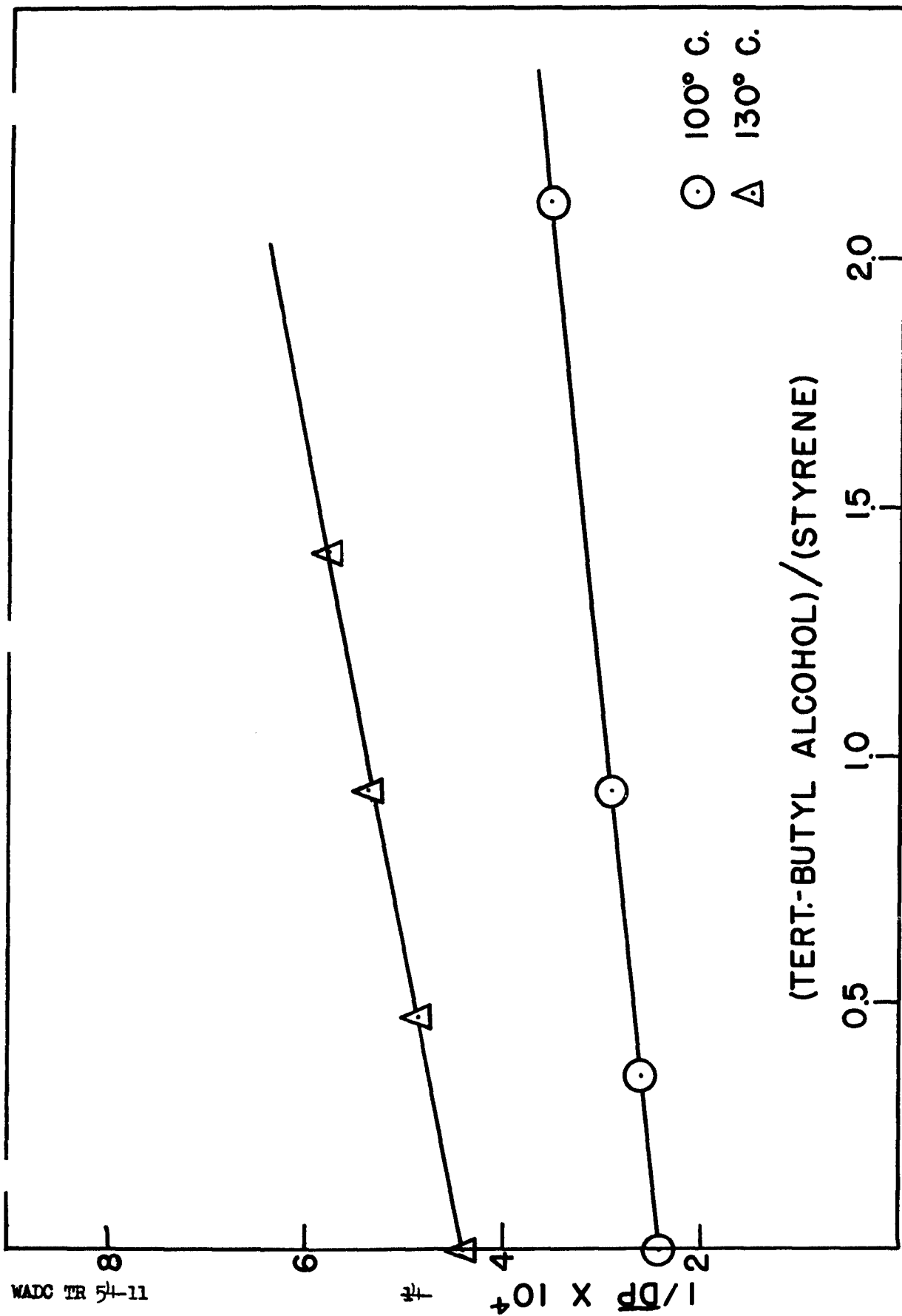


FIG. 3. EFFECT OF TERT-BUTYL ALCOHOL ON THE DP OF STYRENE

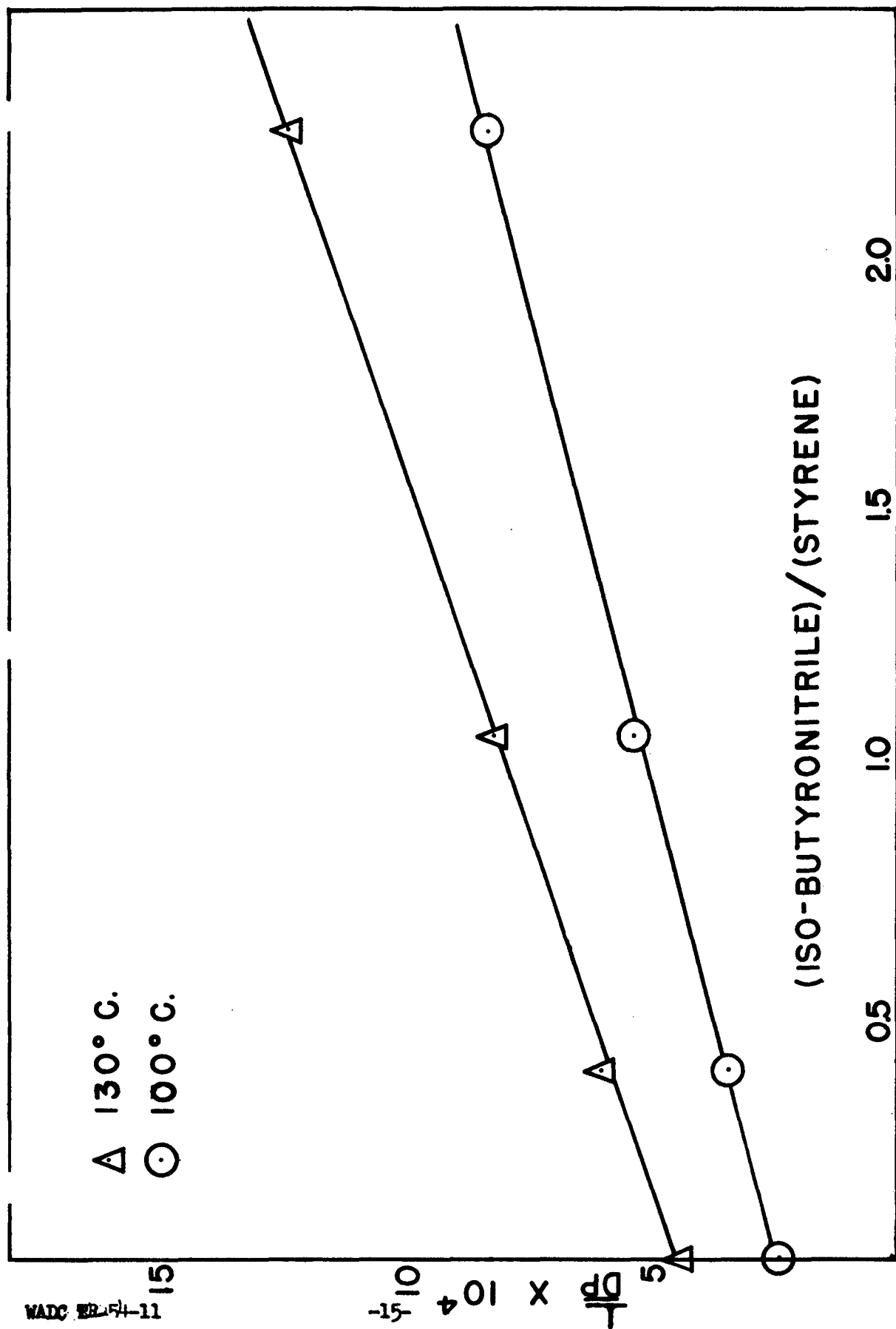


FIG.4. EFFECT OF ISO-BUTYRONITRILE ON THE \overline{DP} OF STYRENE.

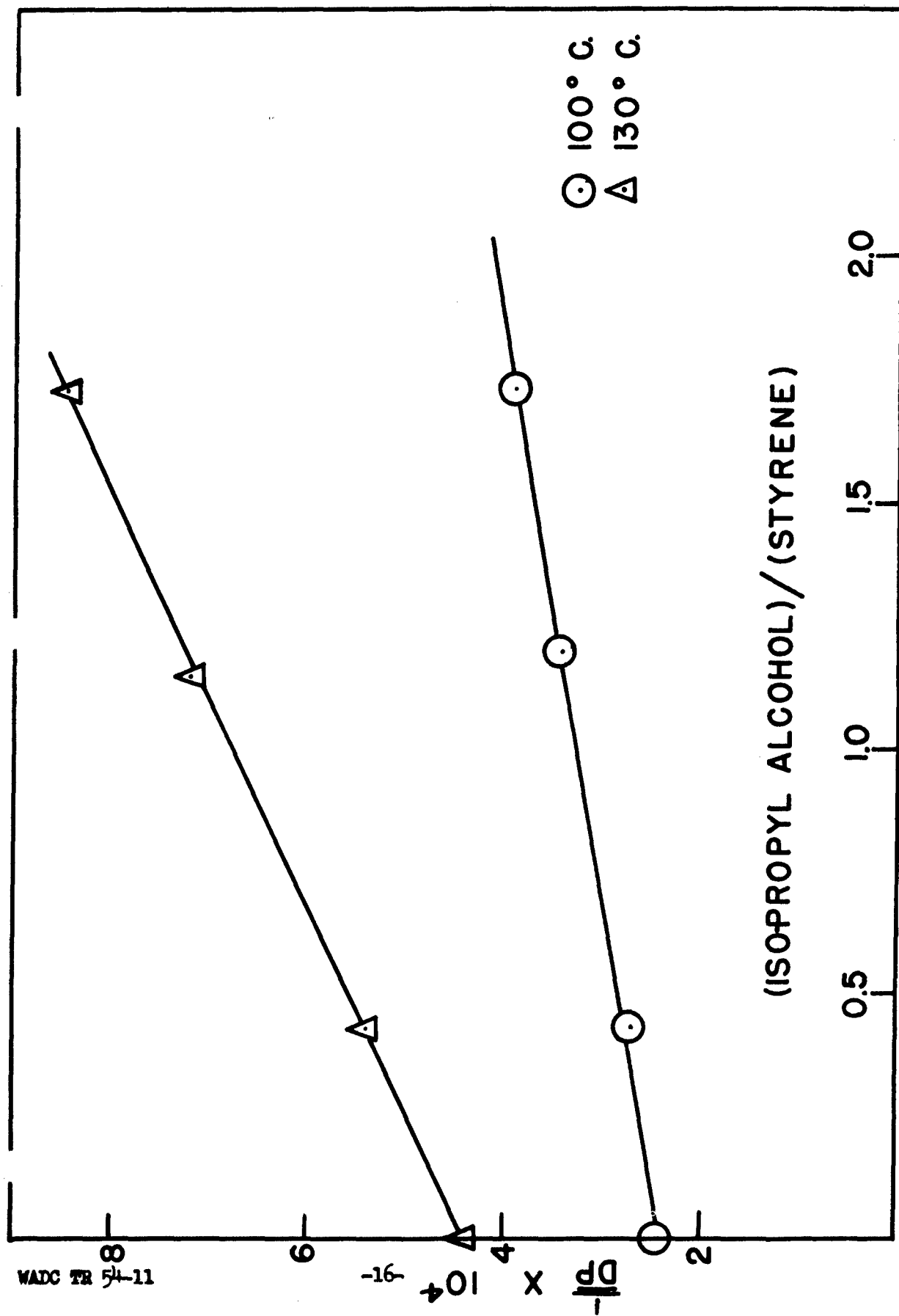


FIG.5. EFFECT OF ISO-PROPYL ALCOHOL ON \overline{DP} OF STYRENE

FIG. 6. EFFECT OF TERT-BUTYL ALCOHOL ON
RATE OF POLYMERIZATION OF STYRENE
AT 130°C.

